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(51) International Patent Classification ⁷ : C08L 23/08, 67/02, 101/00, C08K 5/09, A63B 37/00	A1	(11) International Publication Number: WO 00/23519 (43) International Publication Date: 27 April 2000 (27.04.00)												
(21) International Application Number: PCT/US99/24700 (22) International Filing Date: 21 October 1999 (21.10.99) (30) Priority Data: <table border="0"><tr><td>60/105,065</td><td>21 October 1998 (21.10.98)</td><td>US</td></tr><tr><td>60/105,232</td><td>21 October 1998 (21.10.98)</td><td>US</td></tr><tr><td>60/105,181</td><td>22 October 1998 (22.10.98)</td><td>US</td></tr><tr><td>60/105,193</td><td>22 October 1998 (22.10.98)</td><td>US</td></tr></table> (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: STATZ, Robert, Joseph; 115 Beverly Drive, Kennett Square, PA 19348 (US). CHEN, John, C.; 21 Kent Drive, Hockessin, DE 19707 (US). HAGMAN, John, Francis; 1903 Brant Road, Wilmington, DE 19810 (US). (74) Agent: EVANS, Craig, H.; E.I. Du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		60/105,065	21 October 1998 (21.10.98)	US	60/105,232	21 October 1998 (21.10.98)	US	60/105,181	22 October 1998 (22.10.98)	US	60/105,193	22 October 1998 (22.10.98)	US	(81) Designated States: CA, CH, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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60/105,193	22 October 1998 (22.10.98)	US												
(54) Title: HIGHLY-RESILIENT THERMOPLASTIC ELASTOMER COMPOSITIONS (57) Abstract <p>A thermoplastic composition of (a) a thermoplastic polymer selected from copolyetheresters, elastomeric polyolefins, styrene diene block copolymers, elastomeric polyolefins, thermoplastic polyurethanes and copolyetheramides; (b) a salt of a high molecular weight organic acid; (c) an acid containing copolymer ionomer; and (d) optionally a filler. Also included is use of such compositions in components of one-, two- and three-piece golf balls or multi-layered golf balls made therefrom.</p>														

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TITLE

HIGHLY-RESILIENT THERMOPLASTIC ELASTOMER COMPOSITIONS

BACKGROUND OF THE INVENTION

This application claims the benefit of U.S. Provisional
5 Applications Nos. 60/105,065 and 60/105,232, filed October 21, 1998 and
Nos. 60/105,193 and 60/105,181, filed October 22, 1998.

Field of the Invention

The invention relates to highly-resilient thermoplastic
elastomer compositions, their manufacture and their use as a substitute
10 for thermoset and thermoplastic materials, particularly in the manufacture
of one-, two-, three-piece, and multi-layered golf balls, particularly to
thermoplastic polymer blend compositions useful therein. These
compositions are also useful as foamed materials in footwear and other
sport balls such as softballs.

15 Description of Related Art

Typically, thermoset materials such as polybutadiene rubber,
cross-linked EVA, cross-linked SBS, and cross-linked urethanes have
been used in applications where properties such as resilience, durability,
and low hardness are needed. For example, polybutadiene rubber has
20 traditionally been used in the cores and centers of golf balls.

There currently exist several types of premium golf balls,
particularly three-piece balls, two-piece balls and multi-layered balls.
"Three-piece" balls typically have a spherical molded center, having an
elastomeric thread-like material wound around it, covered with either a
25 thermoplastic or thermoset material. "Two-piece" balls typically have a
spherical molded core covered with a thermoplastic material. "Multi-
layered" balls typically have a core and one or more intermediate layers or
mantles between the core and a cover.

The material used to mold the three-piece centers and the
30 two-piece and multi-layer cores has traditionally been a thermoset rubber
such as polybutadiene rubber. There are, however, major disadvantages

in using thermoset rubbers such as the inability to recycle scrap materials and the need for complex multi-step manufacturing processes. There has been only limited success in attempts to replace the thermoset materials with more-easily-processed thermoplastic materials, the scrap of which
5 can be recycled.

Also, three-piece balls, two-piece balls, and multi-layered balls are by their very nature more complicated and costly to manufacture than the long sought after one-piece golf ball. Attempts to make a premium one-piece ball have heretofore not been successful. Limited-
10 flight range balls, however, have been produced from thermoset rubber and from certain thermoplastic material as set forth in U.S. Patent No. 5,155,157.

U.K. Patent Application 2,164,342A describes one attempt to replace centers and cores and achieve a one-piece golf ball. It teaches
15 moldable compositions comprising ionic copolymers (or potentially ionizable acid copolymers) blended with certain thermoplastic materials such as a polyether block copolyamide, copolyester and the like. Those compositions are said to be useful as three-piece centers, two-piece cores and one-piece solid golf balls, but they lack properties such as durability.
20 Also U.S. 5,155,157 describes a thermoplastic material for cores, centers and one-piece balls. The resins described in this patent can be molded into golf ball parts but the resulting balls are too hard and not resilient enough to perform as a premium golf ball and they are probably too expensive.

25 There still exists the need for a thermoplastic material that is resilient and durable enough with a low enough hardness or compression to be useful as a three-piece center, two-piece core, a one-piece golf ball, and in cores and mantles in a multi-layered golf ball in premium golf balls. Particularly, there is a need for such a material that is not too expensive.

30 SUMMARY OF THE INVENTION

The subject invention provides thermoplastic compositions having high resilience, methods of manufacturing such compositions, and

products made therefrom, such as components of one-, two- and three-piece golf balls or multi-layered golf balls, sport balls and footwear.

More specifically, the thermoplastic composition of this invention comprises a composition comprising (a) a thermoplastic polymer
 5 selected from copolyetheresters, copolyetheramides, block styrene polydiene thermoplastic elastomers, elastomeric polyolefins, and thermoplastic polyurethanes; (b) a salt of a high molecular weight organic acid; (c) a filler (optionally present) and (d) an acid containing copolymer ionomer. Preferable ranges for components (a) through (d) are as set
 10 forth in the following table (percentages are the approximate weight percentages based on the total of the four components, (a) – (d); (d) is always present at a percentage needed to bring total of (a) through (d) to 100%):

	(a)	(b)	(c)
1	1-35%	5-40%	0-60%
2	1-35%	5-40%	Sufficient to raise density to 1.14 – 1.8 gms/cc
3	1-30%	10-30%	Sufficient to raise density to 1.14 – 1.22 gms/cc
4	1-30%	10-30%	15-25%
5	1-25%	15-30%	15-35%
6	1-15%	18-22%	18-22%
7	10-35%	5-10%	Sufficient to raise density to 1.8 gms/cc
8	10-35%	5-10%	40-60%
9	25-35%	5-10%	40-55%
10	28-35%	5-10%	50-55%
11	1-35%	5-30%	0-60%

One embodiment of a product using such composition is a
 15 one-piece golf ball comprising 1-30 weight percent (wt.%) thermoplastic, 10-30 wt.% salt of organic acid, sufficient filler, preferably 15-25 wt.%, to adjust density of ball to 1.14 grams/cubic centimeter (gm/cc), and the remainder to a total 100 wt.% ionomer. Preferably the filler has a density of about 4 gm/cc or greater.

Another embodiment of such a product is a two-piece golf ball having a core and a cover. The core is made of a composition comprising 1-30 wt.% thermoplastic, 10-30 wt.% salt of organic acid, sufficient filler, preferably 15-35 wt.%, to adjust the density of the core to about 1.18 –1.22 gm/cc and the remainder to a total 100 wt.% ionomer. The amount of filler can be adjusted to produce a core with a density varying from the 1.18 gm/cc depending on the diameter of the core and the thickness and composition of the cover to produce a golf ball meeting the weight limits (45 grams) set by the PGA. Preferably the filler has a density of about 4 gm/cc or greater.

Another embodiment is a three-piece golf ball having a center, elastomeric wrapping and a cover. The center is made of a composition comprising 10-35 wt.% thermoplastic, 5-10 wt.% salt of organic acid, sufficient filler, preferably 40-60 wt.% to adjust the density of the center to about 1.8 gm/cc, and the remainder to a total 100 wt.% ionomer. As with the two-piece ball, the amount of filler can be adjusted depending on the size, thickness and composition of the other ball components to produce a golf ball weighing about 45 grams.

Another embodiment is a multi-layer golf ball having a core and a cover with one or more intermediate layers or mantles between the core and the cover. Both the core and the mantle(s) can comprise the composition of this invention. The amount of filler employed in the core and mantle(s) can be varied from 0 to about 60 wt.% depending on the size (thickness) of the components and the desired location of the weight in the ball, provided that the final ball meets the required weight limits. The filler can be used in the core and not in the mantle, in the mantle and not in the core, or in both. Thus, the mantle or the core can comprise about 1-35 wt.% thermoplastic, 5-30 wt.% salt of organic acid, sufficient filler, if needed, to adjust the density to the desired level and the remainder to 100 wt.% ionomer.

As will be appreciated by one skilled in the art, the present invention allows unique golf ball constructions, which are also the subject

of this invention. For example, the weight of the golf ball can be distributed differently than in current golf balls. It is possible to have more weight near the surface of the ball or midway between the center and the surface with a lower density center. It is also possible with the thermoplastic composition of this invention as the core to mold a pattern such as dimples into the core. By doing so, it is possible to obtain a golf ball having a cover with a uniform thickness throughout in contrast to presently available golf balls which have covers that are thinner in the area of the dimples.

10

BRIEF DESCRIPTION OF FIGURES

Figure 1 is a two-dimensional plot of Coefficients of Restitution for one-piece compression-molded golf balls of this invention as determined in an ECHIP study.

15

Figure 2 is a three-dimensional plot of the same information presented in Figure 1.

Figure 3 is a two-dimensional plot of Atti Compression of one-piece compression-molded golf balls of this invention as determined in an ECHIP study.

20

Figure 4 is a three-dimensional plot of the same information presented in Figure 3.

DETAILED DESCRIPTION OF THE INVENTION

Because the species and relative ratios of the components used in the practice of the subject invention vary somewhat, particularly when considered based on the type of golf ball desired (i.e., one-piece, two-piece, three-piece or multi-layered ball), it is useful to first consider the components themselves.

25

All patents set forth herein are incorporated by reference.

COMPONENT DESCRIPTIONS

30

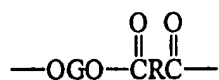
In this disclosure, the term copolymer is used to refer to polymers containing two or more monomers. The term bipolymer or terpolymer refers to polymers containing only two or three monomers

respectively. The phrase 'copolymer of various monomers' means a copolymer whose units are derived from the various monomers.

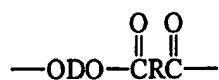
Thermoplastic Polymer

The thermoplastic polymer component of the invention is
 5 selected from copolyetheresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and thermoplastic polyurethanes, these classes of polymers being well known in the art.

The copolyetheresters are discussed in detail in patents
 such as U.S. Patents 3,651,014; 3,766,146; and 3,763,109. They are
 10 comprised of a multiplicity of recurring long chain units and short chain units joined head-to-tail through ester linkages, the long chain units being represented by the formula



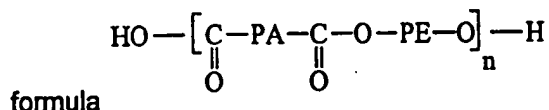
and the short chain units being represented by the
 formula



15 where G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly (alkylene oxide) glycol having a molecular weight of about 400-6000 and a carbon to oxygen ratio of about 2.0-4.3; R is a divalent radical remaining after removal of hydroxyl groups from a dicarboxylic acid having a molecular weight less
 20 than about 300; and D is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight less than about 250; provided said short chain ester units amount to about 15-95 percent by weight of said copolyetherester. The preferred copolyetherester
 25 polymers are those where the polyether segment is obtained by polymerization of tetrahydrofuran and the polyester segment is obtained by polymerization of tetramethylene glycol and phthalic acid. Of course, the more polyether units incorporated into the copolyetherester, the softer the polymer. For purposes of the invention, the molar ether:ester ratio can

vary from 90:10 to 10:90, preferably 80:20 to 60:40; and the shore D hardness is less than 70, preferably less than about 40.

The copolyetheramides are also well known in the art as described in U.S. 4,331,786, for example. They are comprised of a linear
5 and regular chain of rigid polyamide segments and flexible polyether segments, as represented by the general



wherein PA is a linear saturated aliphatic polyamide sequence formed from a lactam or aminoacid having a hydrocarbon chain containing 4 to 14 carbon atoms or
10 from an aliphatic C₆-C₉ diamine, in the presence of a chain-limiting aliphatic carboxylic diacid having 4-20 carbon atoms; said polyamide having an average molecular weight between 300 and 15,000; and PE is a polyoxyalkylene sequence formed from linear or branched aliphatic polyoxyalkylene glycols, mixtures thereof or copolyethers derived
15 therefrom said polyoxyalkylene glycols having a molecular weight of less than or equal to 6000 and n indicates a sufficient number of repeating units so that said polyetheramide copolymer has an intrinsic viscosity of from about 0.8 to about 2.05. The preparation of these polyetheramides comprises the step of reacting a dicarboxylic polyamide, the COOH
20 groups of which are located at the chain ends, with a polyoxyalkylene glycol hydroxylated at the chain ends, in the presence of a catalyst such as a tetra-alkyl ortho-titanate having the general formula Ti(OR)₄, wherein R is a linear branched aliphatic hydrocarbon radical having 1 to 24 carbon atoms. Again, the more polyether units incorporated into the
25 copolyetheramide, the softer the polymer. The ether:amide ratios are as described above for the ether:ester ratios, as is the shore D hardness.

The elastomeric polyolefins are polymers composed of ethylene and higher primary olefins such as propylene, hexene, octene and optionally 1,4 - hexadiene and or ethylidene norbornene or
30 norbornadiene. The elastomeric polyolefins can be functionalized with maleic anhydride.

Thermoplastic polyurethanes are linear or slightly chain branched polymers consisting of hard blocks and soft elastomeric blocks. They are produced by reacting soft hydroxy terminated elastomeric polyethers or polyesters with diisocyanates such as methylene diisocyanate (MDI) or toluene diisocyanate (TDI). These polymers can be chain extended with glycols, diamines, diacids, or amino alcohols. The reaction products of the isocyanates and the alcohols are called urethanes and these blocks are relatively hard and high melting. These hard high melting blocks are responsible for the thermoplastic nature of the polyurethanes.

Block styrene diene copolymers are composed of polystyrene units and polydiene units. The polydiene units are derived from polybutadiene, polyisoprene units or copolymers of these two. In the case of the copolymer it is possible to hydrogenate the polyolefin to give a saturated rubbery backbone segments. These materials are usually referred to as SBS, SIS or SEBS thermoplastic elastomers and they can also be functionalized with maleic anhydride.

Salts of high-molecular-weight organic acid

The salt of organic acid of the present invention comprises the salts, particularly the barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium or calcium salts, of fatty acids, particularly stearic, behenic, erucic, oleic, linoleic. Preferably, the fatty acid salt is selected to have the lowest volatility. It is chosen so as to maximize COR while minimizing Atti Compression, which has often been called "PGA Compression" in the art.

Ionomer

The ionomers of this invention are prepared from 'direct' acid copolymers, that is to say copolymers polymerized by adding all monomers simultaneous, as distinct from a graft copolymer, where a monomer or other unit is grafted onto an existing polymer, often by a subsequent free radical reaction. Methods of preparing ionomers are well known, and are described in U.S. Patent No. 3,264,272 (Rees). Method of

preparing the acid copolymers on which the ionomers are based is described in U.S. Patent No. 4,345,931.

The acid copolymers preferably are alpha olefin, particularly ethylene, C_{3-8} α,β ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, copolymers. They may also contain a third softening monomer such as an alkyl acrylate or methacrylate. The ethylene acid copolymers can be described as an E/X/Y copolymers where E is ethylene, X is the α,β ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, and Y is a softening comonomer such as a C_1 TO C_8 alkyl acrylate or methacrylate ester. X is preferably present in 4-35 (preferably 6-35, most preferably 8-20) weight percent (wt.%) of the polymer, and Y is preferably present in 0-50 (preferably 5-25, most preferably 11-23) weight percent of the polymer.

The acid moiety in the acid copolymer is neutralized about 1 to about 100% (preferably at least 40 to about 100%, most preferably at least about 90 to about 100%) to form an ionomer by a cation such as lithium*, sodium*, potassium, magnesium*, calcium*, barium, lead, tin, zinc* or aluminum (*= preferred), or a combination of such cations.

Specific acid-containing ethylene copolymers include, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/ methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include, ethylene/methacrylic acid/n-butyl acrylate, ethylene/ acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/acrylic acid/ethyl acrylate, ethylene/methacrylic acid/ethyl acrylate, and ethylene/acrylic acid/ methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are, ethylene/(meth)acrylic acid/n-

butyl acrylate, ethylene/(meth)acrylic acid/ethyl acrylate, and ethylene/(meth)acrylic acid/methyl acrylate copolymers.

It has been found that, by adding sufficient organic acid or salt of organic acid to the acid copolymer or ionomer, the ionomer can be neutralized without losing processability to a level above the level that would cause the ionomer alone to become non-melt-processable. That is to say that neutralization of the acid moieties in the acid copolymer from which the ionomer is made to greater than 90%, preferably about 100%, without losing the processability of the ionomer is accomplished by

- (a) melt-blending an ethylene α,β ethylenically unsaturated carboxylic acid copolymer or a melt-processable ionomer thereof with an organic acid or a salt of organic acid, and
- (b) adding a sufficient amount of a cation source to increase the level of neutralization all the acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, (preferably greater than 100%).

Thermoplastic polymer components selected from group consisting of copolyetheresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and thermoplastic polyurethanes, fillers and other ingredients, if included, can be blended in either before, during or after the acid moieties are neutralized to more than 90% or to about 100%. Preferably, fillers (particularly those that react with acid), thermoplastic elastomers and other ingredients are blended in after neutralization to the high level (greater than 90%, preferably about 100%).

Filler

The optional filler component of the subject invention is chosen to impart additional density to blends of the previously described components, the selection being dependent upon the type of golf ball desired (i.e., one-piece, two-piece, three-piece or intermediate layer), as will be more fully detailed below. Generally, the filler will be inorganic having a density greater than about 4 gm/cc, preferably greater than 5

gm/cc, and will be present in amounts between 0 and about 60 wt.% based on the total weight of the composition. Examples of useful fillers include zinc oxide, barium sulfate, lead silicate and tungsten carbide, tin oxide, as well as the other well known corresponding salts and oxides thereof. It is preferred that the filler materials be non-reactive or almost non-reactive with the polymer components described above when the ionomers are less than completely neutralized. If the ionomers are fully neutralized, reactive fillers may be used. Zinc Oxide grades, such as Zinc Oxide, grade XX503R available from Zinc Corporation of America, that do not react with any free acid to cause cross-linking and a drop in MI are preferred, particularly when the ionomer is not fully neutralized.

Other components

Additional optional additives useful in the practice of the subject invention include diacids such as adipic, sebacic or dodecane dioic acid or an acid copolymer wax (e.g., Allied wax AC143 believed to be an ethylene/16-18% acrylic acid copolymer with a number average molecular weight of 2,040) which assist in preventing reaction between the filler materials (such as reactive grades of ZnO) and the acid moiety in the ethylene copolymer. Other optional additives include TiO₂, which is used as a whitening agent or filler; optical brighteners; surfactants; processing aids; etc.

COMBINATIONS OF COMPONENTS

The specific combinations of components used in the practice of the subject invention will in large part be dependent upon the application. The preferred combinations for various types of golf balls (i.e., one-piece, two-piece, three-piece, or multi-layered), are as detailed below.

Three-piece golf ball preferred embodiments

As used herein, the term "three-piece ball" refers to a golf ball comprising a center, a traditional elastomeric winding wound around the center, and a cover made from any traditional golf ball cover material such as Surlyn® ionomer resin, balata rubber or thermoset /thermoplastic

polyurethanes and the like. These three-piece golf balls are manufactured by well known techniques as described in U.S. 4,846,910 for example.

For purposes of this invention, the center of these three-piece balls is made by injection molding of the compositions of this invention. Those centers are placed in a winding machine in which the end of an elastomeric thread is affixed to the molded center and the thread is wound around the center to a predetermined thickness. A dimple-patterned cover is molded around the wound center.

The center is made of a composition comprising 10-35 wt.% (alternatively 25-35 wt.%, preferably 28-35 wt.%) thermoplastic selected from copolyetheramides, copolyetheresters, elastomeric polyolefins, styrenic diene block copolymers or thermoplastic polyurethanes, 5-30 wt.% salt of organic acid, sufficient filler, preferably 40-60 wt.% (alternatively 40-55 wt.% and most preferably 50-55 wt.%) to adjust the density of the center, preferably to about 1.8 gm/cc, so that the total golf ball weight meets specified limits and the remainder to a total 100 wt.% ionomer. The amount of filler (and hence the density of the center) can be adjusted depending on the size, thickness and composition of the other ball components to produce a golf ball weighing about 45 – 46 grams (meet PGA standards).

The preferred thermoplastic component is a copolyetherester. The preferred salt of high molecular weight organic acid is metal salt of stearic, behenic, or erucic acid. The preferred acid-containing ethylene copolymer ionomer is an ethylene/methacrylic acid/normal butyl acrylate or ethylene/acrylic acid/normal butyl acrylate terpolymer.

Two-piece golf ball preferred embodiments

As used herein, the term "two-piece ball" refers to a golf ball comprising a core made from the compositions of the invention, and a cover made from any traditional golf ball cover material as discussed above. These two-piece balls are manufactured by first molding the core from the compositions of the subject invention, positioning these

preformed cores in an injection molding cavity using retractable pins, then injection molding the cover material around the core. Alternatively, covers can be produced by compression molding cover material over the cores.

The core is made of a composition comprising 1-30 wt.%
5 (alternatively 1-25 wt.%, preferably 1-23 wt.%) thermoplastic, 10-30 wt.%
(alternatively 15-30 wt.%, preferably 18-23 wt.%) salt of organic acid,
sufficient filler, preferably 15-35 wt.% (preferably 18-23 wt.%), to adjust
the density of the core, preferably to about 1.18 gm/cc, so that the total
golf ball weight meets specified limits, and the remainder to a total 100
10 wt.% ionomer. The amount of filler can be adjusted to produce a core with
a density varying from the 1.18 gm/cc depending on the diameter of the
core and the thickness and composition of the cover to produce a golf ball
meeting the weight limits (45.93 grams) set by the PGA. Preferably the
filler has a density of about 4 gm/cc or greater, more preferably about 5
15 gm/cc or greater.

The most preferred thermoplastic component is a
copolyetherester. The most preferred acid-containing ethylene copolymer
ionomer is an ethylene /acrylic acid/n-butyl acrylate copolymer ionomer.

The two-piece ball that performs most satisfactorily, as seen
20 in the Examples below, contains a core molded from a composition that
comprises 10-24 wt.% copolyetherester, 20 to 24 wt.% of the magnesium
salt of stearic acid, 45-48 wt.% of an ethylene/(meth)acrylic/n-butyl
acrylate highly neutralized with Mg cations to form the ionomer, and about
22.5% total weight percent ZnO.

25 One-piece golf ball preferred embodiments

As used herein, the term "one-piece ball" refers to a golf ball
molded in toto from the compositions of the subject invention, i.e., not
having elastomeric windings nor a cover. The one-piece molded ball will
have a traditional dimple pattern and may be coated with a urethane
30 lacquer or be painted for appearance purposes, but such a coating and/or
painting will not affect the performance characteristics of the ball. These

one-piece balls are manufactured by direct injection molding techniques or by compression molding techniques.

Preferably a one-piece golf ball comprises 1-30 wt.% (alternatively 1-25 wt.%, more preferably 10-23 wt.%) thermoplastic, 10-30 wt.% (alternatively 15-30 wt.%, more preferably 18-22 wt.% salt of organic acid, sufficient filler, preferably 15-25 wt.% (more preferably 18-22 wt.%), to adjust density of ball to 1.14 grams/cubic centimeter (gm/cc) or to a density that results in a golf ball that does not exceed the limitation on weight of golf ball set by the professional golf governing authority (PGA – 45.93 grams), and the remainder to a total 100 wt.% (c) ionomer. Preferably the filler has a density of about 4 gm/cc or greater, more preferably 5 gm/cc or greater. Density for larger balls (for example, 1.715 inches, 4.3561 cm) will be lower than the 1.14 gms/cc needed to produce a 45.93 gram standard size ball (1.68 inches, 4.2672 cm.). For larger balls, density can be as low as 1.05 gms/cc, for example.

Again, the most preferred thermoplastic component is a copolyetherester. The most preferred metal salt of an organic acid is magnesium stearate, magnesium laurate or magnesium salt of erucic acid. The most preferred acid-containing ethylene copolymer ionomer is an ethylene/acrylic acid/n-butyl acrylate copolymer almost totally neutralized with magnesium cations.

The one-piece balls that perform well, as seen in the Examples below, are molded from compositions of the subject invention comprising about 5-35 wt.% of copolyetherester, 8.5-27 wt.% metal salt of organic acid, 29.5-50 wt.% ethylene/acrylic acid/n-butyl acrylate copolymer highly neutralized with Mg cations to form the ionomer, and about 18 wt.% ZnO.

Multi-Layer golf ball preferred embodiments

As used herein, the term "multi-layer ball" refers to a golf ball comprising a core, a cover made from any traditional golf ball cover material as discussed above, and one or more mantles between the core and the cover. These multi-layer balls are manufactured by first molding or

making the core, typically compression or injection molding a mantle over the core and then compression or injection molding a cover over the mantle.

The multi-layer golf ball having a core and a cover with one or more intermediate layers or mantles between the core and the cover. Both the core and the mantle(s) can comprise the composition of this invention. The amount of filler employed in the core and mantle(s) can be varied from 0 to about 60 wt.% depending on the size (thickness) of the components and the desired location of the weight in the ball, provided that the final ball meets the required weight limits set by PGA (45-46 grams). The filler can be used in the core and not in the mantle, in the mantle and not in the core, or in both. Thus, the mantle or the core can comprise about 1-35 wt.% thermoplastic, 5-30 wt.% salt of organic acid, sufficient filler to adjust the density to the desired level and the remainder to 100 wt.% ionomer. While not intending to be limiting as to possible combinations, this embodiment includes:

1. a core comprising the same composition used in the three-piece center with a mantle made of any composition known in the art,
2. a core comprising the same composition used in the two-piece core or three-piece center with a mantle made of the composition of this invention with or without filler (1-35 wt.% thermoplastic, 5-30 wt.% salt of organic acid, up to 60 wt.% filler (preferably up to 35 wt.%), and the remainder to 100 wt.% ionomer), the total filler in core and mantle adjusted to provide a golf ball of the desired weight, and
3. a core made of any composition (including thermoset compositions such as polybutadiene rubber) with a mantle made of the composition of this invention with or without filler provided that the weight of the finished golf ball meets the required limit.

TESTING CRITERIA

In the Examples set out below, a number of testing criteria are utilized in the evaluation of golf ball performance: percent rebound, coefficient of restitution (COR) and compression.

Percent rebound is determined by dropping the ball (or three-piece center/two-piece core) from a height of 100 inches and measuring the rebound from a hard, rigid surface such as a thick steel plate or a stone block. An acceptable result is about 65-85%.

- 5 COR is measured by firing a golf ball (or two piece core) from an air cannon at a velocity determined by the air pressure. The initial velocity generally employed is between 125 to 180 feet/second. The ball strikes a steel plate positioned three feet away from the point where initial velocity is determined, and rebounds through a speed-monitoring device.
- 10 The return velocity divided by the initial velocity is the COR. Acceptable results are .700 -.810 at 125 ft/sec.

Compression is defined as the resistance to deformation of a golf ball, measured using an Atti machine. An acceptable result is about 70-120.

- 15 Numbers in parentheses in the tables represent the weight percentage of the component in the blend.

TWO PIECE GOLF BALLS PRODUCED WITH THERMOPLASTIC CORES

- 20 These examples describe the preparation of blends for the core for two piece golf balls, golf balls made therefrom, and the properties of the cores and finished balls. The composition of these blends is shown in Table 2. The blends were made using extrusion conditions shown in Table 1A. The blends were molded into cores using conditions shown in Table 1B. The core is 1.53 inches in diameter. Balls were prepared by
- 25 positioning preformed thermoplastic cores in an injection molding cavity. The cores were centrally positioned in the cavity by the use of retractable pins. A cover of mixed Surlyn® ionomer resin was then injection molded around the core. Properties of the resultant cores or balls are shown in Tables 2A and 2B.

TABLE 1A EXTRUSION CONDITIONS FOR TWO PIECE CORES

Screw Speed Rpm	Zone 1 temp °C	Zone 2 temp °C	Zone 3 temp °C	die temp °C	Rate lb./hr.	vacuum m Inches
100-300	150- 170	175- 190	200-220	200-230	15-25	28

TABLE 1B MOLDING CONDITIONS FOR TWO-PIECE CORES

	Temp. °C
Rear	162
Center	176
Front	176
Nozzle	177
Mold Front/Back	21/21
Melt	199

	Pressures Kg/cm ²
Injection 1 st Stage	86
Injection 2 nd Stage	82
Injection 3 rd Stage	47

	Cycle Times (sec)
Hold in 1 st Stage	10
Hold in 2 nd Stage	40
Hold in 3 rd Stage	50
Cure Time	20
Screw Retraction	3.5

5

Screw Speed 150 RPM
 Back Pressure 19 Kg/square cm.
 Mold Diameter 4.01 cm

*Prototype mold, limited cooling, two cavity

10

TABLE 2 CORE COMPOSITIONS

Ex No.	Thermoplastic	Metal salt	Ionomer	Filler
1	H1 (15)	J (20)	B (47)	F3 (18)

2	H1 (10)	J (24)	B (48)	F3 (18)
3	H1 (15)	J (22)	B (45)	F3 (18)

(Percentages given in parenthesis)

B Ethylene , 17 % normal butyl acrylate, 12 % acrylic acid 60 %
neutralized with magnesium ions

H1 Hytrel®3078 polyetherester block copolymer available from
E. I. du Pont de Nemours and Company

F3 Zinc Oxide, grade XX503R available from
Zinc Corporation of America.

J Magnesium stearate available from Witco Corporation

TABLE 2A PROPERTIES of THERMOPLASTIC CORES

Ex No.	M.I. (g/10min)	Atti Compression	Drop Rbn. %	COR @ 125 ft/sec
1	0.53	99	77	.769
2	0.38	102	78.2	.778
3	0.50	97	78.1	.777

TABLE 2B 2-PC. BALL PROPERTIES MADE FROM CORES IN TABLE
2A

Core	Cover	Weight grams	Atti Compression	COR @125ft/sec
1	X	44.5	112	.799
2	X	43.9	114	.806
3	X	44.1	113	.808
Control*	X	45.2	108	.789

5 X - 50/50 blend of ethylene/19% methacrylic acid zinc ionomer about 36%
neutralized and ethylene 19% methacrylic acid sodium ionomer 49%
neutralized.

*The control ball core is a Wilson Ultra polybutadiene core.

10 It can be seen from the data that the thermoplastic cores
give golf balls with a higher resilience then the ball produced from the
Wilson thermoset core.

Examples of One-Piece Golf Balls

Thermoplastic blends of the materials in Table 4 were in general melt homogenized using a 3 inch electrically heated role mill. The blends in examples 5d and 5h were produced by neutralizing the acid copolymer with magnesium 2,4 pentanedionate on a role mill followed by the addition of the other ingredients. The resulting blends when compression molded into one-piece balls had the properties shown in Table 4A.

TABLE 4 ONE PIECE BALL COMPOSITIONS

Ex No	Thermoplastic	Ionomer	Metal salt	Filler
4a	H1(5)	B(50)	J(27)	F3 (18)
4b	H1(20)	B(44.5)	J(17.5)	F3 (18)
4c	H1(35)	B(29.5)	J(17.5)	F3 (18)
4d	H1(15)	B(47)	J(20)	F3 (18)
4e	H1(15)	B(47)	K(20)	F3 (18)
4f	H1(15)	B(47)	L(20)	F3 (18)
4g	H1(15)	B(47)	M(20)	F3 (18)
4h	H1(15)	B(47)	N(20)	F3 (18)
4i	H1(15)	B(47)	O(20)	F3 (18)
5a	H1(15)	B(47)	P(20)	F3 (18)
5b	H1(15)	B(58.5)	Q(8.5)	F3 (18)
5c	H1(15)	B(50)	Q(17)	F3 (18)
5d	H1(15)	C(47)	J(20)	F3 (18)
5e	G(15)	B(47)	J(20)	F3 (18)
5f	H1(15)	B(47)	R(20)	F3 (18)
5g	H1(15)	B(47)	S(20)	F3 (18)
5h	H1(15)	B(47)	J(20)	F3 (18)

10 Ingredients not previously identified are as follows:

- C. Ethylene/ 20% ethyl acrylate/ 5% acrylic acid neutralized 60% with Magnesium.
- G. Pebax® 3533 which is a polyetheramide available from Elf ATO.

- K - magnesium salt of behenic acid prepared by reacting magnesium acetate with behenic acid in an excess of acetic acid under reflux conditions, followed by removing the acetic acid by evaporation.
- L - magnesium salt of oleic acid produced in a manner similar to that
5 for K
- M - sodium salt of Hoechst Wax S (a C₃₆ saturated wax extracted from brown coal).
- N - calcium salt of Hoechst Wax S
- O - lithium salt of Hoechst Wax S
- 10 P - magnesium salt of Hoechst Wax made from Hoechst S in the same manner as the other commercially unavailable salts (see K).
- Q - magnesium salt of dodecanedioic acid made from the acid in manner similar to that for K.
- R - magnesium salt of erucic acid made in a manner similar to that for
15 K
- S - magnesium salt of lauric acid prepared in a manner similar to that of K

TABLE 4A**PROPERTIES OF ONE PIECE BALLS**

Ex No	Atti Compression	COR @ 125 ft/ sec.
4a	89	.781
4b	77	.764
4c	65	.767
4d	79	.771
4e	81	.749
4f	69	.763
4g	108	.733
4h	108	.725
4i	108	.703
5a	102	.705
5b	85	.675
5c	101	.662

5d	51	.731
5e	72	.772
5f	52	.769
5g	76	.782
5h	56	.772

ECHIP DESIGNED EXPERIMENT TO OPTIMIZE COR AND ATTI COMPRESSION

Employing an "experimental design" protocol known as

- 5 ECHIP®, a copyrighted product of Echip Inc., an experimental design was used to evaluate the effects of and interactions between magnesium stearate concentration, ionomer concentration and copolyetherester concentration to determine the effect on compression and coefficient of restitution for one-piece compression-molded golf balls of the three-
- 10 component blend plus 18 wt.% ZnO to adjust density.

From the results displayed in Figures 1, 2, 3 and 4, compositions that exhibit preferred compression and coefficient of restitution can be predicted.

TABLE 5

Ex No.	% Hytrel	% Mg	%	Atti	COR
	H1	Stearate J	Ionomer*	comp.	
6a	35	30%	17	79	.738
6b	5	5	72	80	.718
6c	20	17.5	44.5	77	.770
6d	20	30	32	86	.770
6e	35	5	42	53	.716
6f	5	17.5	59.5	86	.771
6g	35	17.5	29.5	62	.758
6h	5	30	47	86	.792
7a	20	5	57	68	.703
7b	5	5	72	81	.716
7c	35	30	17	75	.746

7d	20	17.5	44.5	74	.762
7e	35	5	42	48	.718
7f	5	30	47	83	.789

Note: All samples contain 18% F3 as the zinc oxide filler to adjust for density.

*E/12AA/17nBA neutralized to 60 % level with Mg cations.

5 RETENTION OF COMPRESSION AND COR VALUES ON ANNEALING SAMPLES

Table 6A shows the results of annealing one piece golf ball formulations at 60°C for 48 hours. These results indicate that, unlike the ion-synergy observed in cover materials, the addition of a metal salt of an organic acid performs better if the ion in the organic acid and the ion in the ionomer are the same.

TABLE 6

Identification	Thermoplastic	Mg Stearate	Ionomer %
8a	H1 (18)	20	B-1(44)
8b	H1 (20)	20	B-1(42)
9a	H1 (15)	20	B (47)
9b	H1 (10)	21	B (50)
9c	H1 (10)	24	B (48)

B-1 is the lithium ionomer produced from E/12AA/17nBA neutralized to 60 % level.

15 TABLE 6A

Ident.	Before Annealing		After Annealing		Delta Comp.	delta COR
	Atti Comp.	COR @125 ft	Atti Comp.	COR @ 125 ft		
8a	118	.739	111	.692	- 7	-.047
8b	115	.743	110	.705	- 5	-.038
9a	72	.782	67	.776	- 5	-.006
9b	72	.787	69	.780	- 3	-.007
9c	79	.788	73	.785	- 6	-.003

CO-NEUTRALIZATION OF FATTY ACIDS AND ETHYLENE ACID COPOLYMERS

Neutralization of acid copolymers and fatty acids at the same time is advantageous as the materials can be neutralized to about 100% neutralization without losing the melt processability associated with ionomers neutralized to greater than 90%. In addition, neutralizing to about 100% reduces the deposits of the fatty acids on the mold vent observed upon molding mixtures with less than 100% neutralization.

Using a Werner & Pfleiderer twin screw extruder it was possible to neutralize the acid copolymer and the stearic acid (or any other fatty acid at the same time. Hence, 4812 grams of stearic acid were added to 7218 grams of an E/23nBA/9.6MAA polymer. Enough magnesium hydroxide (656.3 grams) was added to this mixture to neutralize 70 % of the available acid. The resulting ionomer/fatty acid salt blend had a melt index of 9.0 grams per 10 min (see Ex 17a table 7). Additionally, similar materials with 90 and > 95 % neutralization were prepared in a similar manner (see Ex 17b & 17c)

Two other resins with the composition cited in Table 7 were reacted with stearic acid and magnesium hydroxide. However, in this case, enough magnesium hydroxide was added to neutralize 100% of the available combined acids. These mixed anionic ionomers Ex 18a and 18b are listed in Table 7.

TABLE 7 MAGNESIUM STEARATE MODIFIED MAGNESIUM IONOMERS

Ex No	Resin Comp.	Cation Type	Organic Acid (%)	% Neut	M.I.
17a	E/23nBA/9.6MAA	Mg	Stearic(40)	70	9
17b	E/23nBA/9.6MAA	Mg	Stearic(40)	90	5.2
17c	E/23nBA/9.6MAA	Mg	Stearic(40)	95	3.6
18a	E/15nBA/8.5AA	Mg	Stearic(40)	>100	1.15
18b	E/16nBA/12AA	Mg	Stearic(40)	>100	0.09

Fifty five weight percent of each mixed anionic ionomer was salt and pepper blended with 45 weight percent of a Hytrel®3078/zinc

oxide concentrate containing 50 % zinc oxide. Using a mixing screw on a 6 ounce injection molding machine, spheres 1.524 to 1.531 inches in diameter were molded using the conditions cited in Table 1B. Cores were evaluated for Atti compression and for COR. Table 8 shows the results of these evaluations.

TABLE 8 TWO PIECE CORES PRODUCED FROM SALT and PEPPER BLENDS of IONOMERS 17a-c and POLYETHERESTERS

Ex No	Ionomer/ stearate	Hytrel®/ZnO Concentrate	M.I. of blend	COR@ 125 ft/sec	Atti Comp.	Density
17aa	17a(55%)	45%	1.95	0.752	103	1.16
17bb	17b(55%)	45%	1.89	0.758	92	1.2
17cc	17c(55%)	45%	1.49	0.759	98	1.18

Table 8A shows the results of cores made in the same fashion from the ionomer/stearate blends 18a and 18b.

Table 8A CORES PRODUCED FROM SALTY AND PEPPER BLENDS of IONOMERS 18a & 18b and POLYETHERESTERS

Ex No.	Ionomer/ stearate	Hytrel®/ ZnO Concentrate	COR@125 ft/sec	Compres sion	Density
18aa	18a(55%)	45%	0.768	110	1.18
18bb	18b(55%)	45%	0.782	108	1.19

BLENDS OF FATTY ACID SALTS AND IONOMERS WITH ALTERNATIVE SOFT RESILIENT THERMOPLASTIC ELASTOMERS.

The polyetherester thermoplastic elastomer cited in Examples 1 through 18 can be replaced with a number of alternative soft resilient thermoplastic elastomers. In Examples 11aa through 16bb, we see the results of the use of such blends in cores. All of the blends cited in Tables 9A and 9B were produced by extrusion compounding followed by injection molding. Parenthetical numbers are the weight percent of component in final blend. Conditions cited in Tables 1A and 1B were used to extrusion compound and injection mold for these examples.

TABLE 9A BLENDS OF IONOMERS, FATTY ACID SALTS AND ALTERNATIVE THERMOPLASTIC ELASTOMERS.

Ex No	Ionomer	Fatty acid salt	Elastomer	Proces s Aid	Filler
Control	AA(76.3)	none	None	FF(6.1)	F3(13.8)/EE(3.8)
11-a	AA(55.3)	BB(8.3)	CC(19.3)	FF(4.4)	F3(9.9)/EE(2.8)
12-a	GG(46.3)	BB(19.9)	CC(20.8)	II (0.5)	F3(10.2)/EE(2.3)

12-b	GG(41.4)/HH(13.8)	BB(8.3)	CC(19.3)	FF(4.4)	F3(10)/EE(2.8)
13-a	GG(47.2)	BB(20.6)	JJ(8.3)	None	F3(23.9)
13-b	GG(47.2)	BB(20.6)	KK(8.3)	None	F3(23.9)
13-c	GG(47.2)	BB(20.6)	H1(8.3)	None	F3(23.9)
13-d	GG(47.2)	BB(20.6)	MM(8.3)	None	F3(23.9)
13-e	GG(47.2)	BB(20.6)	NN(8.3)	None	F3(23.9)
control	GG(84.1)	none	none	None	F3(12.95)/ EE(2.95)
14-a	GG(50.0)	OO(21.5)	PP(15)	None	F3(11.0)/EE(2.5)
14-b	GG(41.2)	OO(17.7)	PP(30)	None	F3(9.0)/EE(2.1)
15-a	GG(19.8)/QQ(23)	OO(18.4)	TT(23)	None	F3(15.8)
control	GG(29.4)/RR(29.4)	OO(25.3)	none	None	F3(15.9)
15-b	GG(19.8)/RR(23)	OO(18.4)	TT(23)	None	F3(15.8)
15-c	GG(20)/RR(20)	OO(17.3)	TT(26.7)	None	F3(16)
16-a	GG(20)/SS(24)	OO(16)	TT(16)/UU(5)	None	F3(19)
16-b	GG(20)/QQ(23)	OO(16)	TT(23)	None	F3(18)

Ingredients not previously identified are as follows:

- AA - E/23nBA/9.6 MAA neutralized to about 50 % with zinc cations available from E. I. du Pont de Nemours and Company as Surlyn®9320
- BB - Calcium salt of stearic acid available from Witco Co.
- CC - Nordel®2470 EPDM based on 70% ethylene, 24% propylene, 5.95% 1,4- hexadiene and < .05% norbornadiene available from DuPont Dow Elastomers LLC.
- EE - Titanium dioxide R960 available from E. I. du Pont de Nemours and Company
- FF- Acid-containing ethylene copolymer wax consisting of 85% ethylene and 15% acrylic acid available from Allied Signal as AC143 wax
- GG- E/23 nBA/9.6MAA neutralized to about 50% with magnesium cations available from E. I. du Pont de Nemours and Company as Surlyn®6320.
- HH- Ethylene copolymer ionomer containing 85% ethylene and 15 % methacrylic acid neutralized about 56% with sodium cations and

- available from E. I. du Pont de Nemours and Company as
Surlyn®8945
- II - Adipic acid
- JJ Engage®8180 grafted with 2% maleic anhydride and available from
5 DuPont of Canada as Fusabond®493D
- KK Nordel®IXP3745P grafted with 1.8% maleic anhydride available
from DuPont of Canada as Fusabond®503D5
- MM - An ethylene octene copolymer containing 40% octene produced
with metallocene polymerization catalyst with a 0.5 melt index and
10 a density of 0.863 g/cc. available from the DuPont Dow Elastomers
LLC as Engage®8180
- NN - EPDM elastomer containing 69% ethylene 30.5% propylene 0.5%
norbornadiene produced with a metallocene catalyst and available
from DuPont Dow Elastomers LLC as Nordel®IPX3745P
- 15 OO - Magnesium Stearate available from Witco Co.
- PP - Maleic anhydride grafted block ABA styrene ethylene butene
copolymer available from Shell Chemicals and sold as
Kraton®G1901.
- QQ - Ethylene methacrylic acid copolymer containing 15% methacrylic
20 neutralized about 55% with magnesium ions to an MI of 0.9,
available from E. I. du Pont de Nemours and Company as
Surlyn®6910.
- RR - Ethylene acid copolymer containing 19 % methacrylic acid
neutralized 37% with sodium ions, available from E. I. du Pont de
25 Nemours and Company as Surlyn®8140.
- SS - Ethylene acid copolymer containing copolymer containing 19%
methacrylic acid 40% neutralized with magnesium ions to an MI of
1.1, available from E. I. du Pont de Nemours and Company as
Surlyn®6120.
- 30 TT - EPDM elastomer containing 71% ethylene 28.5% propylene, 0.5%
norbornene produced with a metallocene catalyst and available
from DuPont Dow Elastomer LLC as Nordel®IPX3720P.

UU - Maleic anhydride grafted copolymer containing 0.9% maleic anhydride grafted on to an ethylene copolymer containing 30% propylene available from DuPont of Canada as Fusabond®MF416D

5 TABLE 9B RESULTS ON SPHERES MOLDED FROM COMPOSITIONS CITED IN TABLE 9A

Ex No	Atti comp,	COR@125 ft/sec
control	81	0.629
11-a	83	0.709
12-a	73	0.725
12-b	91	0.715
13-a	126	0.736
13-b	119	0.738
13-c	129	0.741
13-d	124	0.741
13-e	123	0.742
control	72	0.669
14-a	67	0.740
14-b	54	0.700
15-a	95	0.735
control	140	0.743
15-b	119	0.738
15-c	108	0.719
16-a	61	0.731
16-b	95	0.735

CLAIMS

1. A composition comprising
about 1 to about 35 wt.% component (a), a thermoplastic
elastomer selected from copolyetheramides, copolyetheresters,
5 elastomeric polyolefins, block polystyrene polydiene copolymers, and
thermoplastic polyurethanes,
about 5 to about 40 wt.% component (b), a salt of organic
acid,
from 0 to about 60 wt.% component (c), a filler, and
10 the remainder to a total 100 wt.% of the components (a)
through (d) of component (d), an ionomer.
2. The composition of claim 1 wherein component (c) is
selected and in an amount sufficient to adjust the density of the
composition to a range of from about 1.14 to about 1.8 gm/cc.
- 15 3. The composition of claim 2 wherein (a) is about 1 to
about 30 wt.%, (b) is about 10 to about 30 wt.%, (c) is sufficient to adjust
the density of the composition to a range of about 1.14 to about 1.22
gm/cc, and (d) is the remainder to a total 100 wt.% of the components (a)
through (d).
- 20 4. The composition of claim 2 or 3 wherein the (c) has a
density of about 4 gm/cc or greater and is about 15 to about 25 wt.% of
the total of components (a) through (d).
5. The composition of claim 2 or 3 wherein (a) is about 1 to
about 25 wt.%, (b) is about 15 to about 30 wt.%, (c) has a density of at
25 least 4 grams/cubic centimeter and is about 15 to about 35 wt.% and (d) is
the remainder to a total 100 wt.% of the components (a) through (d).
6. The composition of claim 5 wherein (a) is about 1 to
about 15 wt.%, (b) is about 18 to about 22 wt.%, (c) is about 18 to about
22 wt.%, and (d) is the remainder to a total 100 wt.% of the components
30 (a) through (d).
7. The composition of claim 2 wherein (a) is about 10 to
about 35 wt.%, (b) is about 5 to about 10 wt.%, (c) is sufficient to adjust

the density of the composition to about 1.8 gm/cc, and (d) is the remainder to a total 100 wt.% of the components (a) through (d).

8. The composition of claim 7 wherein (c) has a density of about 4 gm/cc or greater and is about 40 to about 60 wt.% of the total of
5 components (a) through (d).

9. The composition of claim 8 wherein (a) is about 25 to about 35 wt.%, (b) is about 5 to about 10 wt.%, (c) is about 40 to about 55 wt.%, and (d) is the remainder to a total 100 wt.% of the components a) through d).

10. The composition of claim 9 wherein (a) is about 28 to about 35 wt.%, (b) is about 5 to about 10 wt.%, (c) is about 50 to about 55 wt.%, and (d) is the remainder to a total 100 wt.% of the components a) through d).

11. A one-piece golf ball comprised of a composition
15 selected from those of claim 2 wherein the filler is sufficient to adjust the density to a level that results in a golf ball meeting the weight limits set by the professional golf governing authority.

12. The one-piece golf ball of claim 11 wherein (a) the thermoplastic polymer is a polyetherester having a shore D hardness of
20 about 40, (b) the salt of organic acid is a magnesium salt of stearic acid, (c) filler is ZnO, and (d) the ionomer is an ethylene/(meth)acrylic/n-butyl acrylate highly neutralized with Mg cations.

13. A two-piece golf ball comprised of a core and a cover wherein the core comprises a composition selected from those of claim 1
25 where the filler is sufficient to adjust the density of the core to about 1.18 gm/cc.

14. The two-piece golf ball of claim 13 wherein the core comprises (a) thermoplastic polymer that is a polyetherester having a shore D hardness of about 40, (b) salt of the organic acid that is a salt of
30 stearic acid; (c) filler that is selected from ZnO and BaSO₄, and (d) the ionomer is a partially neutralized ethylene/alkyl (meth)acrylate/(meth)acrylic acid copolymer.

15. The two-piece golf ball of claim 14 wherein the salt of stearic acid is a magnesium salt, the ionomer is an ethylene/(meth)acrylic acid/n-butyl acrylate highly neutralized with Mg cations to form the ionomer, and the filler is ZnO.

5 16. The two-piece golf ball of claim 13 wherein the core has a dimple pattern such that when positioned in the ball and covered by the cover having a dimple pattern, the cover thickness in the dimple areas is the about the same as the dimple thickness in the non-dimpled areas.

10 17. A three piece golf ball comprised of a center, an elastomeric winding and a cover wherein the center comprises a composition selected from those of claim 7.

15 18. The three-piece golf ball of claim 17 wherein (a) thermoplastic elastomer is a copolyetherester having a shore D hardness of 40, (b) metal salt of the organic acid is a magnesium salt of stearic acid, (c) filler is ZnO, and (d) ionomer is an ethylene/acrylate ester/acrylic acid (12%) copolymer highly neutralized with Mg cation.

20 19. A multi-layer golf ball having a core and a cover with one or more intermediate layers or mantles between the core and the cover, the core and the mantles being independently or both made from the compositions of claim 2 wherein the filler is sufficient to adjust the density of the core or mantle or both in which the composition is used to a level such that the golf ball has a density of 1.14 gms/cc.

25 20. The multi-layer golf ball of claim 19 wherein the mantle(s) and the core independently or both comprise about 1 to about 35 wt.% (a), about 5 to about 30 wt.%(b), up to 60 wt.%(c), and the remainder to 100 wt.% (d).

30 21. A process to make a thermoplastic elastomer composition comprising the steps of
 (a) melt-blending an ethylene α,β ethylenically unsaturated carboxylic acid copolymer or a melt-processable ionomer thereof with an organic acid or a salt of organic acid, and

(b) concurrently or subsequently adding sufficient cation source to neutralize more than 90% of all the acid moieties.

22. The process of claim 21 wherein about 100% of the acid moieties are neutralized.

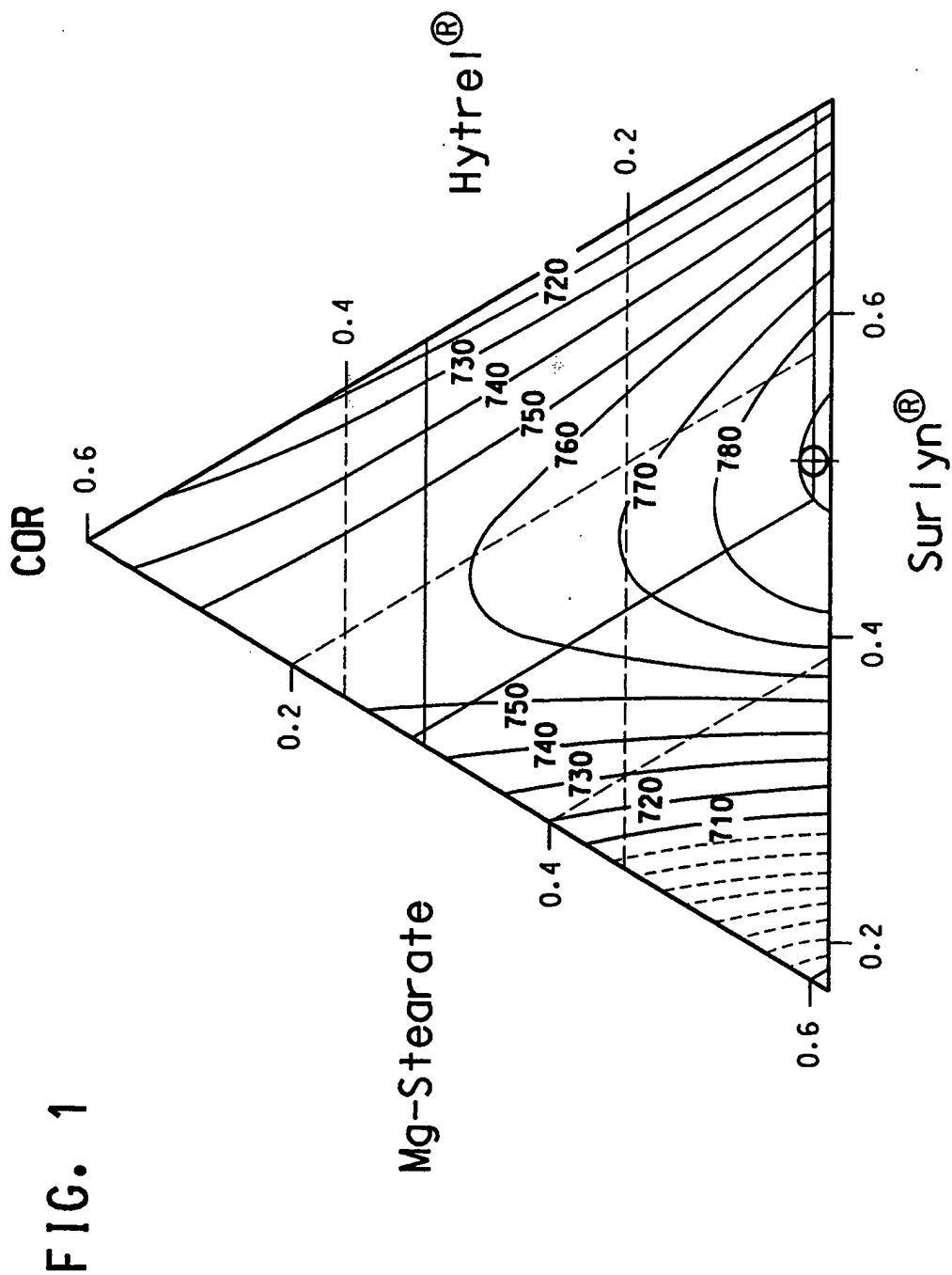
5 23. The process of claim 21 further comprising blending in a thermoplastic polymer component selected from group consisting of copolyetheresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and thermoplastic polyurethanes.

10 24. The process of claim 21 or 23 further comprising blending in a filler.

25. The process of claim 23 wherein the thermoplastic polymer component is added after neutralization to greater than 90%.

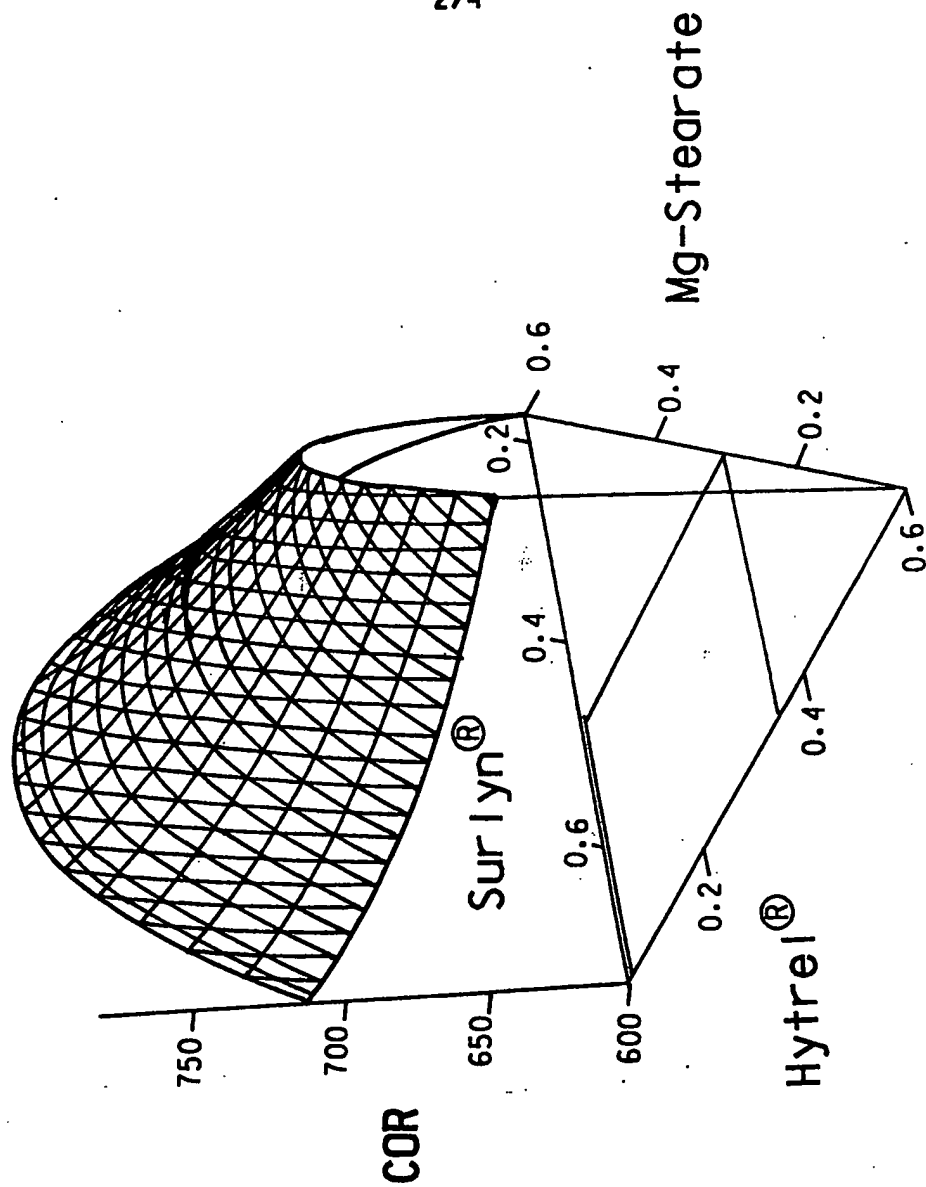
26. The process of claim 24 wherein the filler is not reactive with acid moieties.

15 27. The process of claim 24 wherein the filler is added after neutralization to greater than 90%.

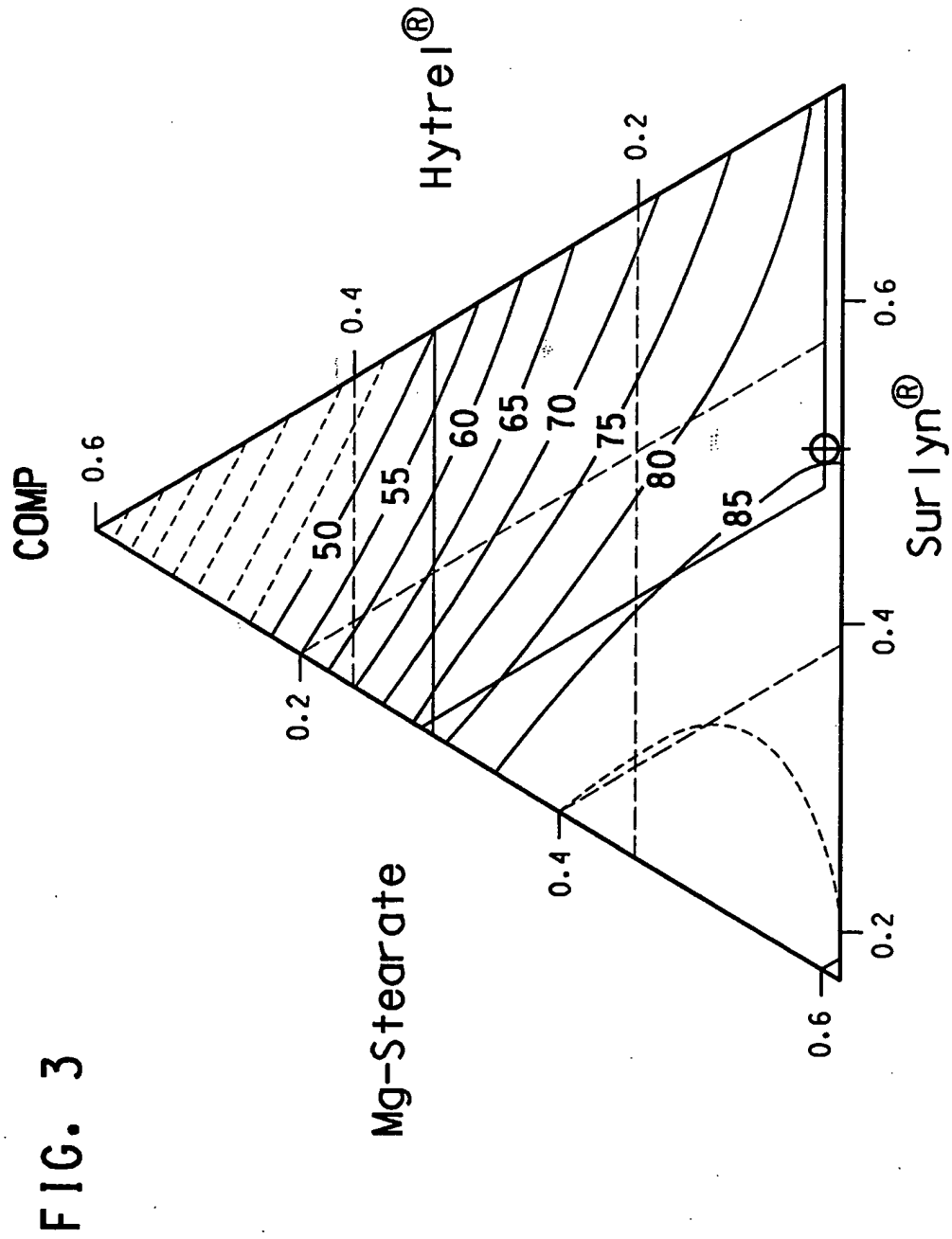


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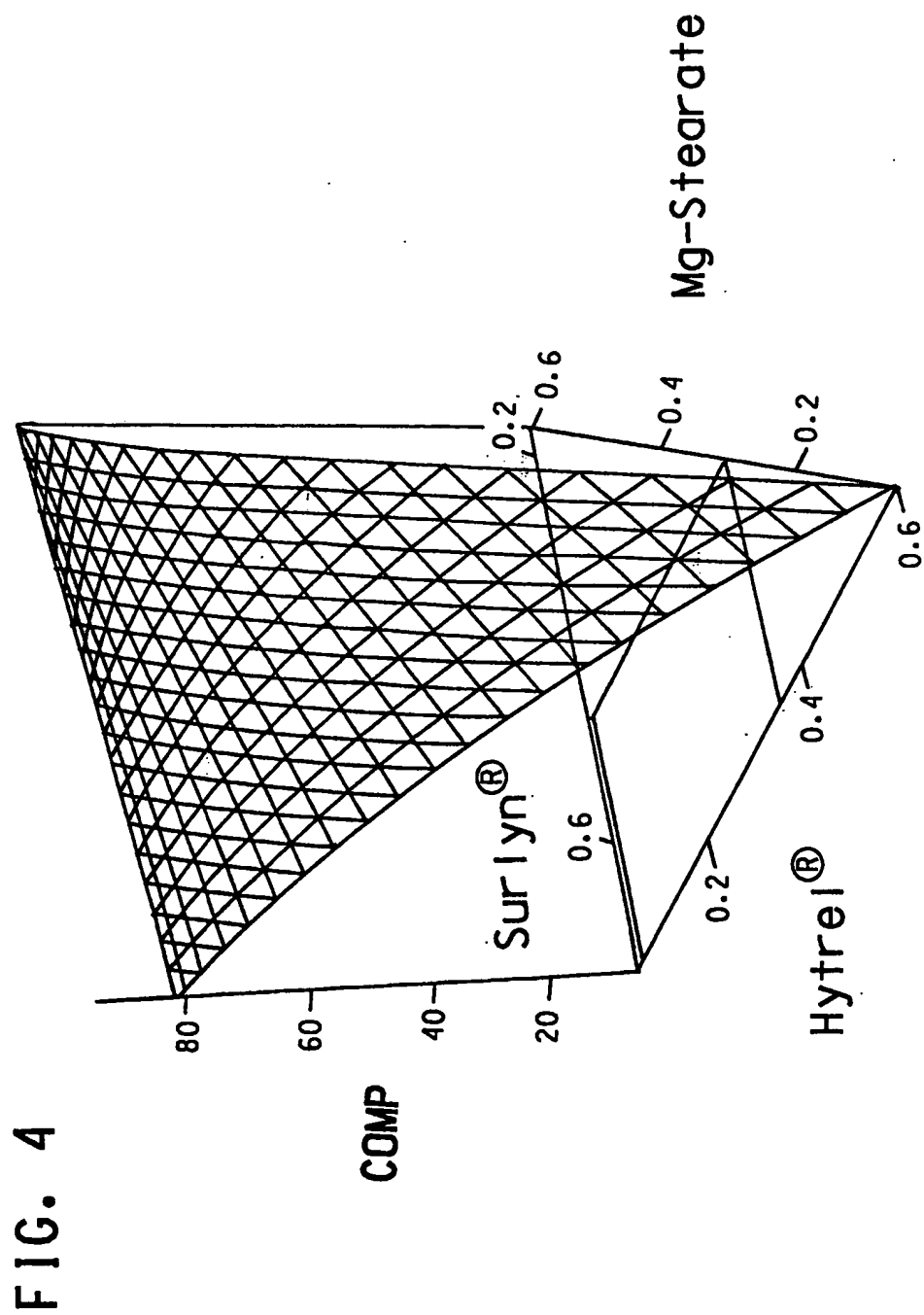
FIG. 2



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INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08L23/08 C08L67/02 C08L101/00 C08K5/09 A63B37/00		Intl. Appl. No. PCT/US 99/24700
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08L C08K A63B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 129, no. 12, 21 September 1998 (1998-09-21) Columbus, Ohio, US; abstract no. 149996, XP002131233 abstract & JP 10 219053 A (YOKOHAMA RUBBER CO.) 18 August 1998 (1998-08-18)	1
Y	WO 92 12206 A (DU PONT) 23 July 1992 (1992-07-23) claims 1-34 page 7, line 3 -page 8, line 29 & US 5 155 157 A cited in the application	1-15, 17-20
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
Date of the actual completion of the international search 22 February 2000		Date of mailing of the international search report 09/03/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Krische, D

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/24700

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 339 743 A (SHELL INT RESEARCH) 2 November 1989 (1989-11-02) abstract page 3, line 16 -page 4, line 18 ---	1-15, 17-20
P,Y	WO 98 46671 A (DU PONT) 22 October 1998 (1998-10-22) claims 1,2; tables 1,4,5 page 1, line 14 -page 4, line 2 page 10, line 1 - line 30 ---	1-15, 17-20
Y	GB 2 168 059 A (SPALDING & EVENFLO) 11 June 1986 (1986-06-11) claim 1; example ---	1
Y	US 5 306 760 A (SULLIVAN MICHAEL J) 26 April 1994 (1994-04-26) claims 1-4 column 4, line 18 - line 65 column 5, line 36 -column 6, line 9 ---	1
Y	GB 2 164 342 A (DUNLOP LTD) 19 March 1986 (1986-03-19) cited in the application claims 1-17; examples 2-6 ---	1,2,4,11
Y	DATABASE WPI Section Ch, Week 199810 Derwent Publications Ltd., London, GB; Class A23, AN 1998-103921 XP002131234 & JP 09 221581 A (TEIJIN LTD), 26 August 1997 (1997-08-26) abstract ---	1,2,4,11
Y	US 3 384 612 A (BRANDT, HARRY W. ET AL) 21 May 1968 (1968-05-21) claim 1; examples I,II,IV ---	1,2,4,11
Y	BE 699 171 A (FARBENFABRIKEN BAYER AG) 3 November 1967 (1967-11-03) claim; examples 1,5-7 page 3, paragraph 4 -page 6, paragraph 1 page 9, paragraph 3 -page 10, paragraph 3 page 12, paragraph 2 -page 13, paragraph 2 ---	1,2,4,11
X	WO 98 03565 A (HENKEL CORP) 29 January 1998 (1998-01-29) claim 11; example 7 page 5, line 16 - line 20 ---	21,22
	-/--	

INTERNATIONAL SEARCH REPORT

In .ational Application No

PCT/US 99/24700

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>ANTONY, PRINCE ET AL.: PLASTICS, RUBBER AND COMPOSITES PROCESSING AND APPLICATIONS, vol. 26, no. 7, 1997, pages 311-317, XP000864417 page 311 -page 312 page 317</p> <p>-----</p>	1,21-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Jonal Application No

PCT/US 99/24700

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10219053 A	18-08-1998	NONE	
WO 9212206 A	23-07-1992	AU 659122 B AU 9150091 A CA 2099269 A DE 69118207 D DE 69118207 T EP 0564560 A ES 2086115 T JP 6504308 T SG 49887 A US 5155157 A	11-05-1995 17-08-1992 28-06-1992 25-04-1996 31-10-1996 13-10-1993 16-06-1996 19-05-1994 15-06-1998 13-10-1992
EP 0339743 A	02-11-1989	AU 609971 B AU 3370589 A JP 1313546 A US 4921914 A US 4970268 A	09-05-1991 02-11-1989 19-12-1989 01-05-1990 13-11-1990
WO 9846671 A	22-10-1998	EP 0909291 A	21-04-1999
GB 2168059 A	11-06-1986	AU 4942685 A CA 1266144 A DE 3541892 A ES 549517 A FR 2574419 A IE 57172 B IT 1183006 B JP 61149178 A SE 8505838 A US 4674751 A ZA 8508578 A	19-06-1986 20-02-1990 12-06-1986 01-12-1986 13-06-1986 20-05-1992 05-10-1987 07-07-1986 11-06-1986 23-06-1987 29-07-1987
US 5306760 A	26-04-1994	US 5312857 A	17-05-1994
GB 2164342 A	19-03-1986	JP 61072042 A ZA 8505717 A	14-04-1986 25-03-1987
JP 9221581 A	26-08-1997	NONE	
US 3384612 A	21-05-1968	NONE	
BE 699171 A	03-11-1967	DE 1255305 B FR 1528995 A GB 1113409 A	15-10-1968
WO 9803565 A	29-01-1998	NONE	

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